

# Synopsis

Name of the Candidate	P MARIA NIRMAL RAJAKUMARI
Degree Registered	M Sc (Engg )
S R No	5628/93
Thesis title	<b>Network formation in amine curing of higher functional epoxy resins.</b>
Research Supervisor	Prof Manas Chanda, Dept of Chemical Engineering Indian Institute of Science, Bangalore - 560 012

---

High performance epoxy systems that retain their properties to high temperatures are usually made up of one or more multi-functional epoxies and are cured in presence of multi-functional amines. Curing is the process by which linear epoxy resins are converted into three-dimensional network. The physical and mechanical properties of the cured thermosets are dependent on the chemical reactions that take place during cure. The variety of reactions involved during the cure cycle of the epoxy system makes the detailed theoretical determination of the network structure quite complex and in most cases intractable. Also majority of high performance epoxy systems are quite rigid and insoluble in most solvents thus eliminating the use of direct experimental procedures for the determination of fundamental network parameters like molecular weight, and crosslink density. Thus we have to go in for theoretical techniques which can provide information about the network indirectly.

Several statistical methods have been developed so far to describe the curing of epoxy-amine systems. From the literature, it is clear that the work done so far has been limited upto diepoxies. Nowadays, higher functional epoxy resins like triepoxy and tetraepoxy resins find wide applications in aerospace, electronics, automotive and other industries. Hence tri and tetra functional epoxy resins have been taken up for the present work, and models have been developed for curing of these resins with diamines.

Curing mechanism of epoxy-amine reaction involves three types of reactions. They are epoxy-primary amine reaction, epoxy-secondary amine reaction and epoxy-hydroxyl group reaction (etherification). There is considerable contradiction in literature on whether etherification reaction takes place or not. Hence the models developed in the present work considers both curing in the presence as well as in the absence of etherification.

Though a number of models are available in the literature, the methods chosen

for the present study are the statistical structural fragment approach developed by Riccardi and Williams, and the recursive approach developed by Macosko and Miller. In the fragment model, different structural fragments are generated based on the possible curing reactions. These fragments are able to denote the unreacted species as well as the larger molecules emerging as a consequence of polymerization. A kinetic scheme accounting for the evolution of all the fragments is developed. This together with a simple expectation theory is used to find the pregel properties such as weight-average molecular weight and post gel properties such as sol, pendant chain and elastic material fractions for curing of triepoxy and tetraepoxy resins using diamines. All the properties have been calculated for the cases where epoxy and amine are taken in stoichiometric proportions as well as in nonstoichiometric proportions (where, for example, epoxy is 100% in excess over amine).

The expressions derived by the statistical structural fragment approach are solved for triglycidyl para-amino phenol (TGPAP) – 3,4 toluene diamine (TDA) and tetraglycidyl diamino diphenylmethane (TGDDM) – 2,6 pyridine diamine (PDA) systems. All the properties derived are plotted as a function of epoxy conversion. From these plots, a comparison is made of curing in the presence of etherification and in the absence of etherification as well as of curing with epoxy and amine in stoichiometric and nonstoichiometric proportions and the results are discussed in detail. Triepoxy and tetraepoxy curing has been compared and the results have been analyzed.

In the recursive approach, the average properties of the network can be calculated directly. It utilizes the simple elementary probability and recursive nature of the network polymers. From the model equations derived by the recursive approach, molecular weight, sol fraction and crosslink density have been calculated as a function of epoxy conversion. The results have been presented in the form of graphs and compared with the results of the aforesaid fragment model. The two models are found to be in good agreement.